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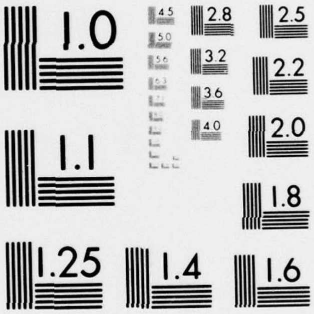
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APPLICATION OF ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY TO THE ANALYSIS OF CONTAMINANTS IN FUELS AND LUBRICANTS

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AFLRL No. 102

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by

Marvin K. Greenberg

and

Frank M. Newman

prepared by

U.S. Army Fuels and Lubricants Research Laboratory
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A rapid and inexpensive x-ray fluorescence spectroscopic method for the analysis of particulate contaminants has been developed. The method employs the collection of the particulates by filtration followed by x-ray fluorescence analysis of the filter. A unique method for the preparation of standard materials on filters for calibration of the x-ray spectrometer has been developed. Linear response over 2 orders of magnitude is routine. The sensitivity is in the parts per million range. The precision and accuracy is about 3 to 5 percent.

The method is currently being used to determine contamination in fuels and to correlate the contamination and wear metal particulates in lubricants with engine wear. A large number of turbine

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fuels and lubricants have been analyzed and the data obtained have correlated to field performance.

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INTRODUCTION

The need to determine the quantity and nature of contaminants in fuels and lubricants frequently arises. The elemental composition is necessary to establish origin of the contaminant or the degree of engine wear. This aids in the elimination of the contamination and the minimization of catastrophic engine failures which might occur.

APPROACH

A rapid and inexpensive method employing an energy dispersive X-ray fluorescence spectrometer has been developed. An advantage of energy dispersive X-ray fluorescence analysis is the ability to simultaneously analyze for virtually every element with a Z number greater than that of sodium. The developed method requires the collection of the particulates on filters followed by X-ray fluorescence analysis of these filters. The decision to use a filtration technique was based on the need to minimize various factors hindering the analysis of the fuels and lubricants on an "as is" basis. These factors are:

(1) variable matrix effects due to the varying physical properties of the fuels and lubricants;

(2) reduction of sensitivity produced by X-ray absorption in the matrix;

(3) inter-element effects such as enhancement and absorption, and

(4) self-absorption effects.

By collecting the particulates on a filter, thus separating the analyte from the fluid matrix, fluid matrix effects are eliminated. There is also a significant increase in sensitivity because the particles are concentrated on the filter surface, free of the absorption effects on both the incident and emitted X-rays.

EXPERIMENTAL

When the method was first developed, a standard 47-mm membrane filtration apparatus was used with filters of 0.45 μm porosity. By exposing a piece of photographic film to the X-ray beam, we determined that the diameter of the X-ray beam was 32 mm, which was smaller than the 35-mm deposit diameter obtained from the standard filtration apparatus. Some of the deposit was outside the beam and not being analyzed. A stainless-steel funnel for the filtration apparatus was designed to produce a 25-mm diameter filter deposit which was totally covered by the X-ray beam, and the sensitivity was increased significantly.

When using the filtration method, other factors are encountered which must be controlled. They are:

(1) self-absorption due to particle size;

(2) self-absorption due to the thickness of the layer deposited, and

(3) the uniformity of deposit.

These factors have a major effect on the precision of the analysis. If the particle size of the particulates is greater than 2 μm, self-absorption problems will occur. In such cases, the sample is filtered or centrifuged, and the particulates weighed. The particulates are then hand ground to a particle size less than 2 μm. A portion of the ground particulates is weighed and suspended in an appropriate fluid. An aliquot is taken and filtered for analysis. If the original material is a solid sample and not in a fuel or lubricant, it may be ground and the same filter deposition procedure followed.

When the deposit on the filter is too thick or is nonuniformly deposited, self-absorption may occur, producing erroneous results. To control the deposit thickness, a volume of sample is filtered which will produce a deposit weighing less than 2 mg. Nonuniformity is prevented by adding an appropriate solvent such as water or heptane to the funnel before addition of sample in order to keep the particulate material suspended until filtration. It has been found that when these factors are controlled, inter-element effects become negligible.

STANDARDIZATION

A unique method for the preparation of standard materials on filters for calibration of the X-ray spectrometer has been developed. The materials used for the standard filter preparation were water-insoluble compounds. When standards were being prepared, compounds were selected to minimize interelement effects. Oxides and carbonates were chosen wherever possible. An example of the type of compound used is $CaCO_3$. The carbon and oxygen of the carbonate ion are low Z elements with minimum X-ray absorption properties and do not interfere significantly.

To prepare a standard, the material must be thoroughly ground to less than 2 μm so that there will be no self-absorption effect due to particle size. The solid must be suspended in a suitable fluid such as heptane or, preferably, water. For the suspension of the solid, an appropriate volumetric flask is three-quarters filled with the fluid. One drop of wetting agent, such as Triton X-100, is added to the solvent to facilitate dispersion and suspension of the solid material. If water is the solvent, a drop of binding agent, such as a white glue, is added to the flask to prevent the material from flaking off the filter. The flask is placed in an ultrasonic cleaner to agitate the fluid. The solid material is added. The agitation helps in dispersing the material uniformly throughout the fluid and eliminates agglomerates. The flask is filled to the mark, and an aliquot taken for filtration. The filter in the funnel is prewetted and covered by 20 to 40 ml of the same type fluid into which the sample has been dispersed, and the aliquot is added. This prevents localized spotting on the filter which would produce nonuniform deposits. The wet filter with its unrinsed deposit is placed in an oven at approximately 100°C for 30 seconds and then air dried.

RESULTS

Fluorescent X-ray production is linearly proportional to the weight of element up to 0.10 mg of element. See Figure 1. Above 0.10 mg, some deviation from linearity is observed. See Figure 2. The sensitivity of the analysis is in the microgram range with a precision of about 3 to 5 percent. When applied to fluids analysis, parts per million to parts per billion sensitivities are possible, depending on the amount of original fluid filtered. A unique and powerful technique has been developed for the analysis of particulate contaminants in fuels and lubricants. A precise and accurate

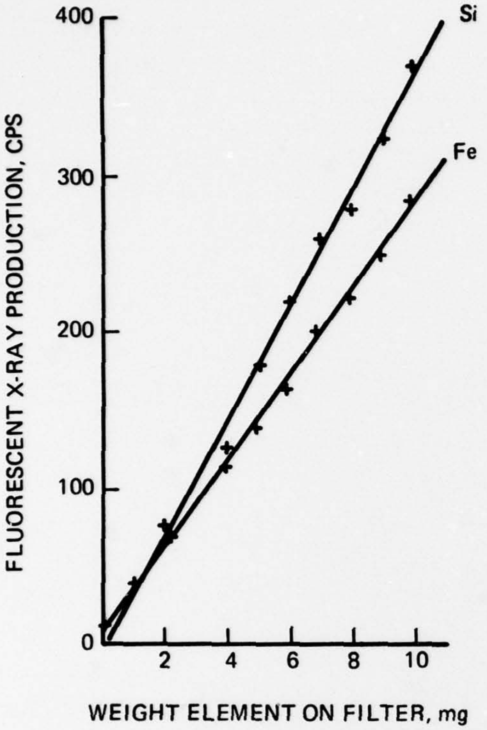

FIGURE 1. CALIBRATION CURVES FOR TWO ELEMENTS

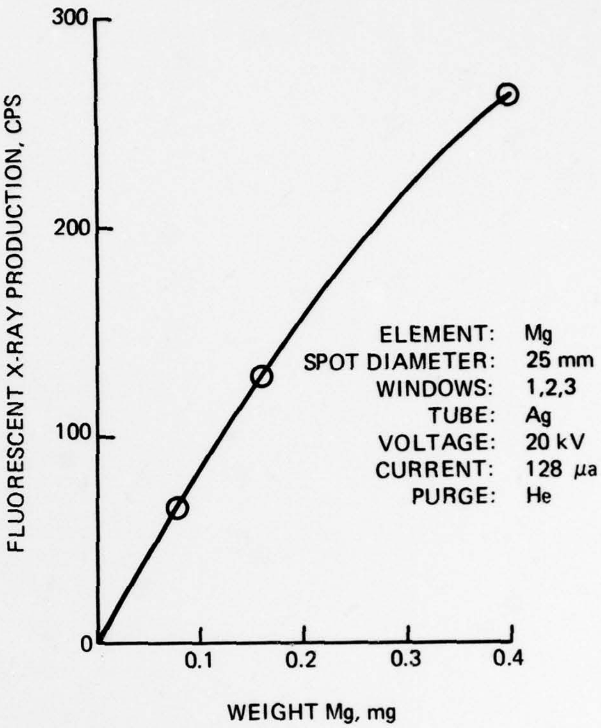

FIGURE 2. CALIBRATION CURVE SHOWING DEVIATION FROM LINEARITY

method has been developed for the preparation of standards on fine porosity filters. This methodology has been successfully applied to a large number of samples from a wide variety of sources.(1, 2) It has been found to be a very capable method.

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(2) Unpublished analytical data of more than 2000 turbine engine oil samples from engines; performed for AMRDL, Fort Eustis, Virginia.

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